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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

In re Application of

Applicant: JEAN-YVES CHENARD ET AL : Group 143

Serial No.: 254,313 : Examiner:
V. Hoke

Filed: April 15, 1981 :

For: IMPROVEMENT IN THE STABILIZATION
OF VINYL HALIDE POLYMERS

DECLARATION OF M. FOURE -- 37 CFR 1.132

Hon. Commissioner of Patents and Trademarks
Washington, D. C. 20231

Sir:

I, MICHEL FOURE, do hereby declare that:

1. I am a Doctor Rerum Natur in Chemistry; this degree was conferred on me by the State University of Wurzburg (West Germany) in 1975; I did post-doctorate research in chemistry at the University of Osaka (Japan) from 1975-1977;
2. I was employed at the Lacq, France, Research Centre of Societe Nationale Elf Aquitaine from 1977 to 1980, doing research in cosmetics and fragrances, lubricants, process development, organotin biocides and polyvinyl chloride stabilizers; in 1980 I became employed by M&T Chemicals Inc., at Rahway, New Jersey, as a Research Associat in th ir Polyvinyl Chloride (PVC) Additives Group; in 1981 I was promoted to the position of Manager, PVC Additives Group; I hold fiv patents in the field of stabilization of PVC;

3. I am intimately familiar with the invention of Chenard, et. al. relating to the use of certain mercaptoesters in conjunction with an organotin stabilizer to stabilize polyvinyl chloride with respect to heat. I am also familiar with the patents relied on by the Examiner to reject the Chenard, et. al. application.
4. The following experiments were carried out under my direction and supervision; they were designed to compare the compositions claimed in the Chenard, et. al. application with the compositions described in the prior art with respect to heat stabilization of polyvinyl chloride.

Since the major basis of the Examiner's rejection was the Gough and Stapfer references, I selected the following sulfur compounds from Examples 20 to 27 of Gough (Table III page 13 of U.S. 3,928,285):

isooctyl-thioglycolate
isooctyl β -mercaptopropionate
octadecylthioglycolate
n-butylthioglycolate
dodecylmercaptan
benzylthioglycolate*
octylmercaptan

*This sulfur compound became available only toward the end of the study.

From Stapfer, I selected the preferred product:

thiolauric anhydride

From Chenard, et. al., I selected the following mercaptoesters as representative:

- mercaptoethyl tallate (oleate/linoleate)
- mercaptoethyl pelargonate (C9)
- mercaptoethyl ester of C108 fatty acid
- mercaptoethyl stearate
- mercaptoethyl succinate

The organotin stabilizers were selected to represent different classes of materials; additionally, I included a boron-containing tin compound disclosed by Gough.

A masterbatch containing the following formulation was dry blended:

	<u>Parts by Wt.</u>
PVC (suspension grade)	100.0
Calcium Carbonate	3.0
Titanium Dioxide	1.0
Calcium Stearate	0.5
Paraffin Wax	0.8

Stabilizers were added to the masterbatch and sheets were prepared by milling the composition on a 2-roll mill for 5 minutes at 350°F. The sheets were removed and specimens 2x3 in. were cut out. Six of these 2x3 in. sheets (i.e., samples of six different formulations) were placed in an aluminum mold and heated at 350°F and 40,000 PSI for 10 minutes. Readings of the whiteness index (WI) for each 2x3 in. rectangle were taken directly from a Macbeth MC 1500 S colorimeter; the readings were rounded to the nearest tenth. Sample results are reproducible to ± 1 unit.

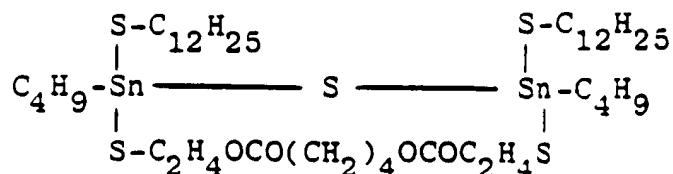
The level of sulfur compound was chosen to be comparable to Gough; I used 0.3 parts per hundred while Gough used 0.33 phr.

In evaluating the test results, I considered a difference of 3 units to be important; this degree of difference indicates that the results are not equivalent. I consider a difference of 5 or more units to be significant; this degree of difference indicates a substantial superiority of one formulation over another.

The results of each experiment are presented graphically. In each case the value of the Whiteness Index without a sulfur compound is subtracted from the values obtained with a sulfur compound to normalize the relative improvement (or decline) in performance provided by the sulfur compound.

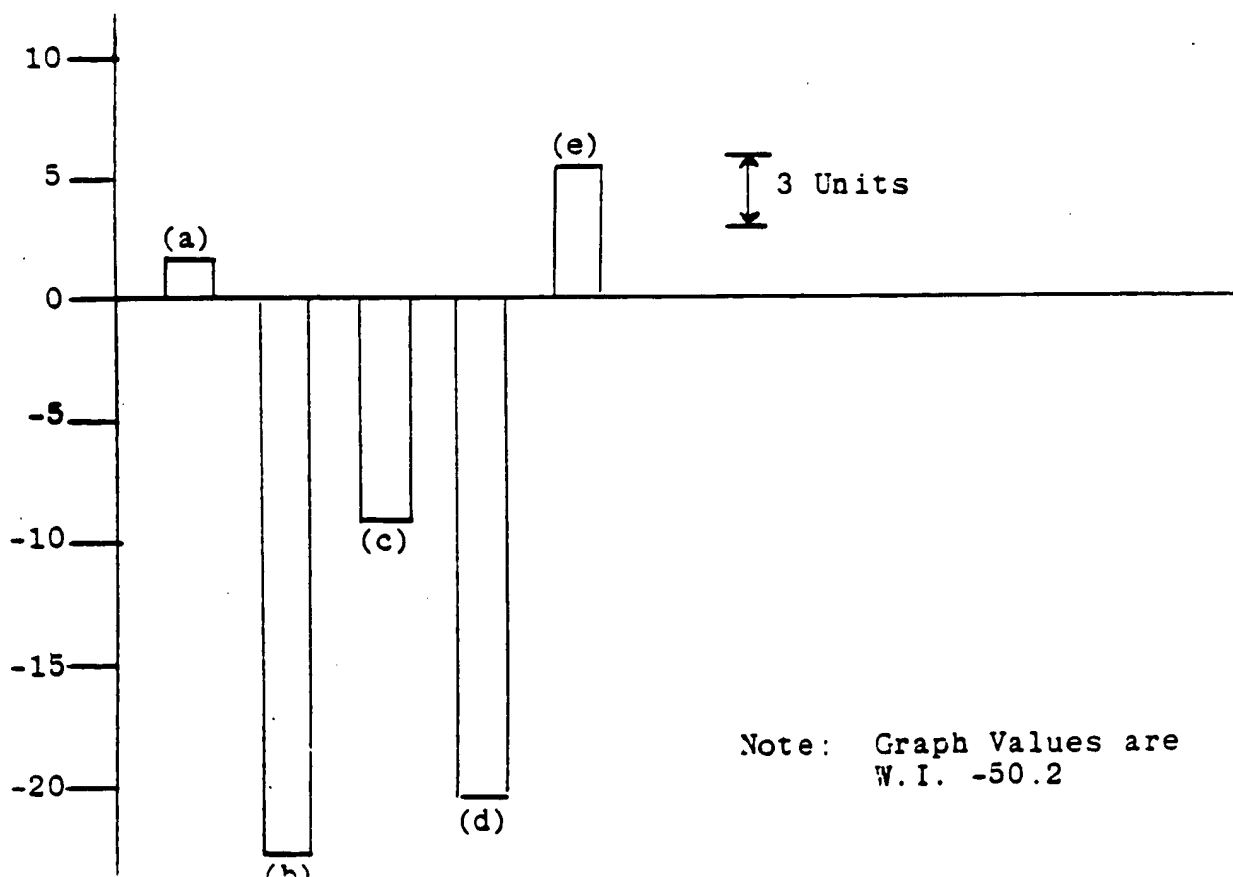
EXPERIMENT 1

Tin Stabilizer: Contains 22.1% Tin



<u>TIN</u> <u>STABILIZER</u>	<u>SULFUR COMPOUND</u>	<u>AMT.</u>	<u>WI</u>
0.15 phr	--	0.0 phr	50.2
0.15 phr	diisooctylthiodipropionate (a)	0.3 phr	51.9
0.15 phr	n-decylmercaptoacetate (b)	0.3 phr	27.3
0.15 phr	cyclohexylmercaptan (c)	0.3 phr	41.2
0.15 phr	thiolauric anhydride (d)	0.3 phr	29.4
0.15 phr	mercaptoethyl tallate (e)	0.3 phr	56.0

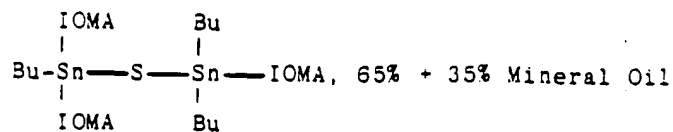
Most of the sulfur compounds degraded performance; the mercaptoethyl tallate displays a significant improvement over the other sulfur compounds.



Note: Graph Values are
W.I. -50.2

EXPERIMENT 2

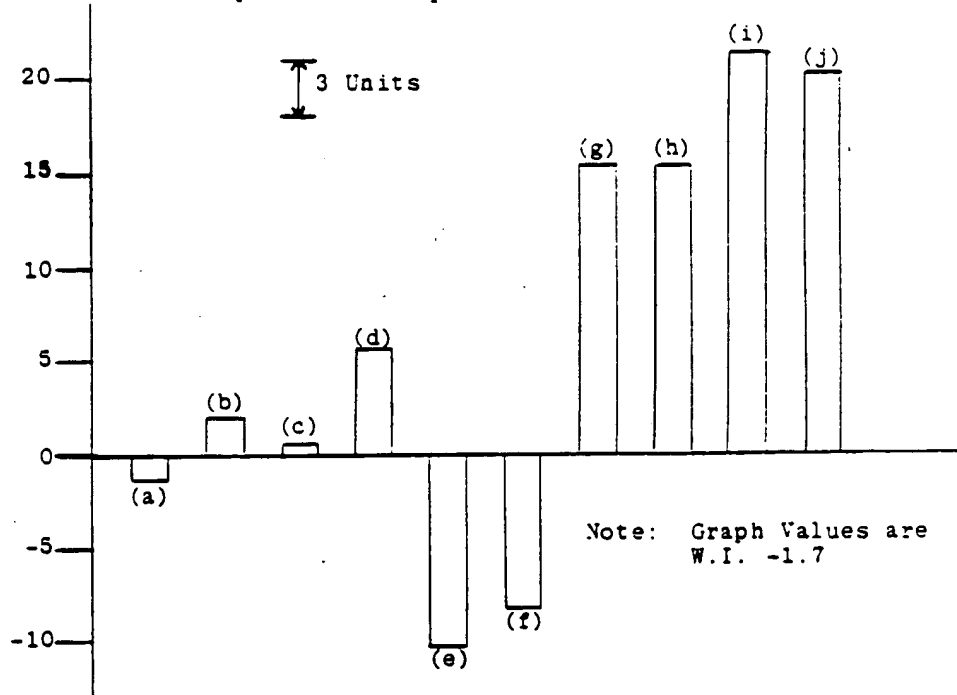
Tin Stabilizer: Contains 14.5% Tin



IOMA = isooctylmercaptoacetate

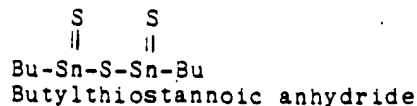
TIN STABILIZER	SULFUR COMPOUND	AMT.	WI
0.15 phr	--	0.0 phr	1.7
0.15 phr	i-octylmercaptoacetate	(a) 0.3 phr	0.4
0.15 phr	i-octyl-3-mercaptopropionate	(b) 0.3 phr	3.7
0.15 phr	octadecylthioglycolate	(c) 0.3 phr	2.3
0.15 phr	n-butylthioglycolate	(d) 0.3 phr	7.4
0.15 phr	dodecylmercaptan	(e) 0.3 phr	-8.7
0.15 phr	octylmercaptan	(f) 0.3 phr	-6.5
0.15 phr	benzylthioglycolate	(g) 0.3 phr	16.9
0.15 phr	thiolauric anhydride	(h) 0.3 phr	16.9
0.15 phr	mercaptoethyl stearate	(i) 0.3 phr	22.9
0.15 phr	mercaptoethyl succinate	(j) 0.3 phr	22.1

In my opinion, the results obtained with the Chenard, et. al. mercaptoesters are significantly superior to the results obtained with prior art compounds.



EXPERIMENT 3

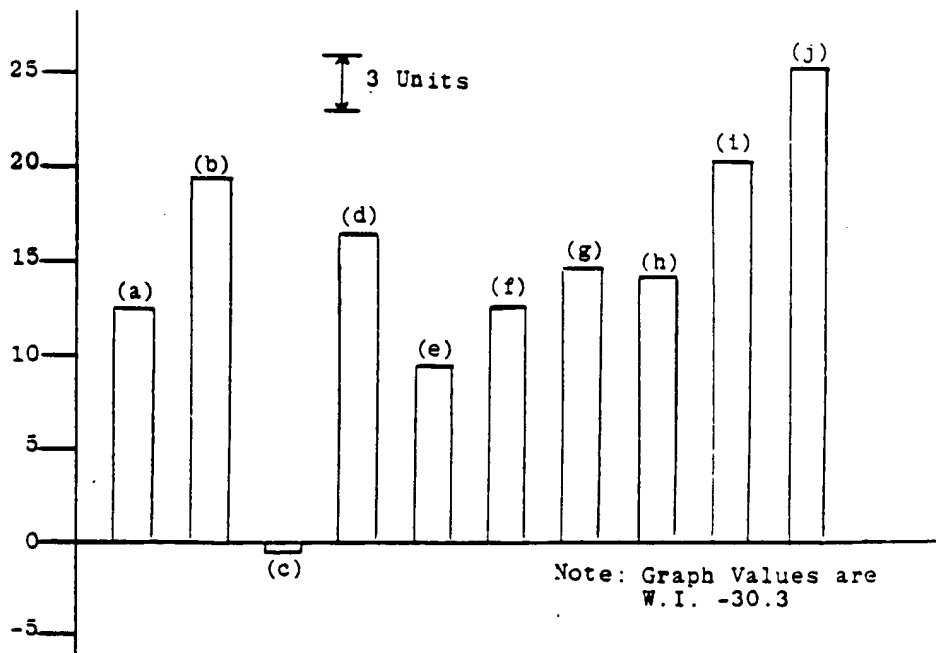
Tin Stabilizer: Contains 53.1% Tin



<u>TIN</u> <u>STABILIZER</u>	<u>SULFUR COMPOUND</u>	<u>AMT.</u>	<u>WI</u>
0.10 phr	--	0.0 phr	30.3
0.10 phr	i-octylthioglycolate	(a) 0.3 phr	42.5
0.10 phr	i-octyl g-mercaptopropionate	(b) 0.3 phr	49.5
0.10 phr	octadecylthioglycolate	(c) 0.3 phr	29.7
0.10 phr	n-butylthioglycolate	(d) 0.3 phr	46.7
0.10 phr	dodecylmercaptan	(e) 0.3 phr	39.8
0.10 phr	octylmercaptan	(f) 0.3 phr	42.9
0.10 phr	benzylthioglycolate	(g) 0.3 phr	45.0
0.10 phr	thiolauric anhydride	(h) 0.3 phr	*44.5
0.10 phr	mercaptoethyl stearate	(i) 0.3 phr	50.4
0.10 phr	mercaptoethyl succinate	(j) 0.3 phr	55.6

*(Brown Shade)

In my opinion, the results with the Chenard, et. al. mercaptoesters are significantly above those obtained with the compounds of the prior art.



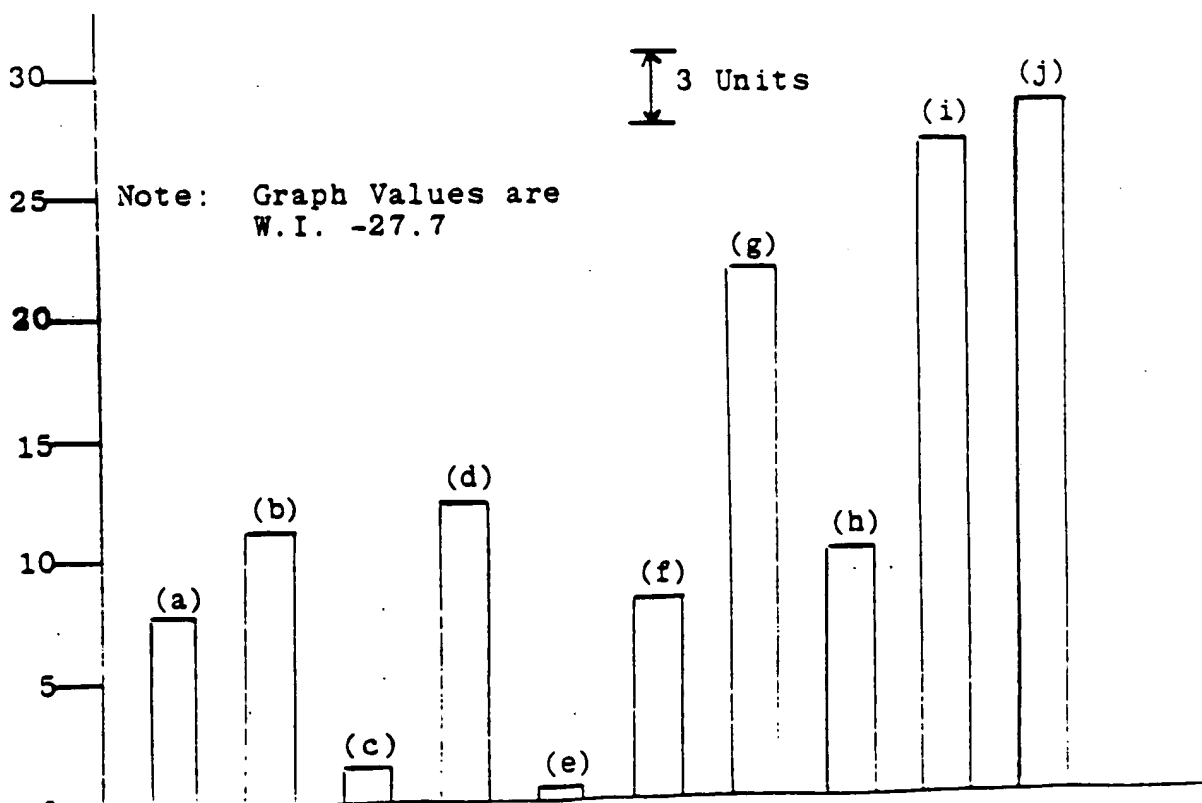
EXPERIMENT 4

Tin Stabilizer: Contains 29.0% Tin

$\text{BuSn(S)SCH}_2\text{CO}_2\text{C}_8\text{H}_{17}$
 Monobutyltin(isooctylmercaptoacetate)sulfide

<u>TIN</u> <u>STABILIZER</u>	<u>SULFUR COMPOUND</u>	<u>AMT.</u>	<u>WI</u>
0.15 phr	--	0.0 phr	27.7
0.15 phr	isooctylthioglycolate	(a) 0.3 phr	35.6
0.15 phr	isooctyl β -mercaptopropionate	(b) 0.3 phr	38.8
0.15 phr	octadecylthioglycolate	(c) 0.3 phr	29.0
0.15 phr	n-butylthioglycolate	(d) 0.3 phr	40.0
0.15 phr	dodecylmercaptan	(e) 0.3 phr	28.4
0.15 phr	octylmercaptan	(f) 0.3 phr	36.0
0.15 phr	benzylthioglycolate	(g) 0.3 phr	49.7
0.15 phr	thiolauric anhydride	(h) 0.3 phr	38.0
0.15 phr	mercaptoethyl stearate	(i) 0.3 phr	54.8
0.15 phr	mercaptoethyl succinate	(j) 0.3 phr	56.7

I consider the results obtained with the Chenard, et. al. mercaptoesters to be significantly superior to those obtained with the prior art compounds.



EXPERIMENT 5

Tin Stabilizer: Contains 29.1% Tin

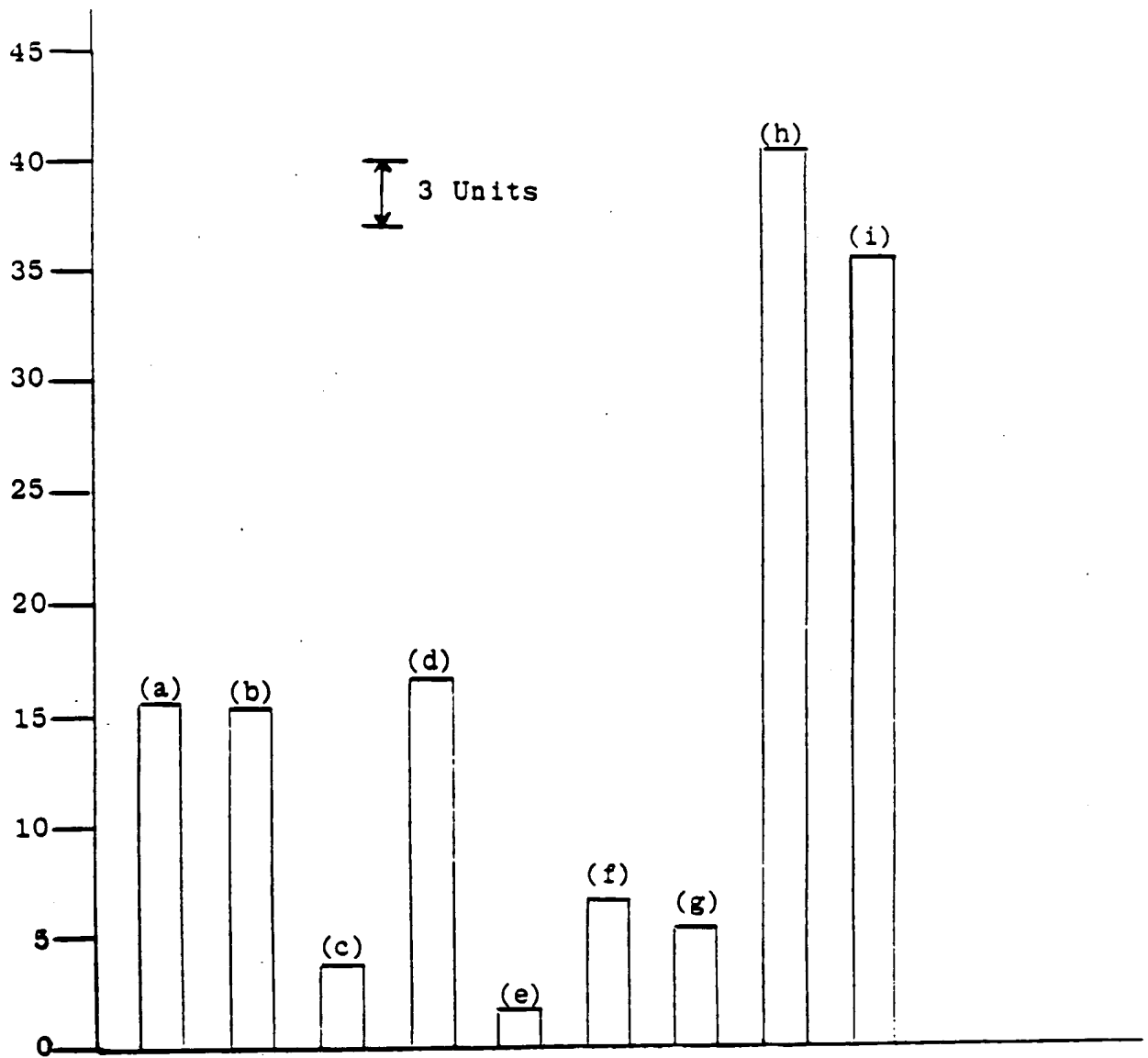
$\text{BuSn(S)SC}_{12}\text{H}_{25}$
Monobutyltin(sulfide)(dodecylmercaptide)

<u>TIN</u> <u>STABILIZER</u>	<u>SULFUR COMPOUND</u>	<u>AMT.</u>	<u>WI</u>
0.15 phr	--	0.0 phr	24.1
0.15 phr	isooctylthioglycolate	(a) 0.3 phr	39.9
0.15 phr	isooctyl β -mercaptopropionate	(b) 0.3 phr	39.7
0.15 phr	octadecylthioglycolate	(c) 0.3 phr	28.0
0.15 phr	n-butylthioglycolate	(d) 0.3 phr	41.0
0.15 phr	dodecylmercaptan	(e) 0.3 phr	25.9
0.15 phr	octylmercaptan	(f) 0.3 phr	31.0
0.15 phr	thiolauric anhydride	(g) 0.3 phr	29.2
0.15 phr	mercaptoethylpelargonate	(h) 0.3 phr	64.4
0.15 phr	*mercaptoethyl-C108 acid ester	(i) 0.3 phr	59.9

*C108 is a coconut-based mixed C₈-C₁₄ fatty acid obtained from the Proctor & Gamble Corp.

It is seen that the mercaptoesters of Chenard, et. al. improve performance to an extent approaching an order of magnitude above the prior art.

EXPERIMENT 5 - CONT'D



Note: Graph Values are
W.I. -24.1

EXPERIMENT 6

Tin Stabilizer: Contains 31.0% Tin

1,3-bis(4,4,6-trimethyl-1,3,2-dioxaborinyl-2-oxy)
(tetra-n-butyldistannoxane)

This is the product a-1 (Ex 1) in Gough U.S. 3,928,285; it is used in examples 20 to 27 (Table III, pl3). The limited availability of this product (lab sample) forced me to select only the best sulfur compounds as indicated by Gough in Table III.

<u>TIN</u> <u>STABILIZER</u>	<u>SULFUR COMPOUND</u>	<u>AMT.</u>	<u>WI</u>
0.15 phr	--	0.3 phr	deep purple
0.15 phr	i-octylthioglycolate	0.3 phr	-20.2
0.15 phr	i-octyl β -mercaptopropionate	0.3 phr	5.4
0.15 phr	n-butylthioglycolate	0.3 phr	- 7.5
0.15 phr	benzylthioglycolate	0.3 phr	10.9
0.15 phr	octylmercaptan	0.3 phr	-10.8
0.15 phr	thiolauric anhydride	0.3 phr	-25.9

The organotin borate alone has almost no stabilizing effect despite a tin content comparable to experiments 4 and 5, above. This is in full agreement with Gough's results (compare examples 12 and 27 of Gough). Thus, almost anything can improve the performance of the organotin borate.

5. On the basis of the experiments described above, it is my opinion that the results obtained with the compositions of Chenard, et. al. are consistently superior to a substantial degree over those of the prior art; further, it is my opinion that those results could not be predicted from the prior art.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

8-18-1982

Date _____



MICHEL FOURE